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## Nanocomposite Electrodes for Advanced Lithium Batteries: The $\text{LiFePO}_4$ Cathode

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### ABSTRACT

$\text{LiFePO}_4$  was successfully synthesized by high temperature and hydrothermal synthesis. A nanocomposite was formed by carbon coating this material; initial electrochemical results showed that up to 70% capacity could be obtained at  $1.0 \text{ mA/cm}^2$  current density. In contrast, the hydrothermally prepared  $\text{LiFePO}_4$  showed a lower capacity even at lower discharge rates due to a partial occupation of lithium sites by iron. This occupation, identified by Rietveld X-ray refinement, decreased both the rate and degree of intercalation and de-intercalation of lithium; chemical reaction with butyl lithium and bromine confirmed the electrochemical behavior. This investigation showed that the cathode could be prepared by high temperature synthesis, followed by a carbon black coating to achieve high capacity at high current density.

### INTRODUCTION

$\text{LiFePO}_4$  has been of much interest recently [1-3] due to its low cost, high performance and stability. Its theoretical capacity is  $170 \text{ mAh/g}$ , 40% more than that of the  $\text{Li}_x\text{CoO}_2$  presently used in commercial batteries, where  $\Delta x \approx 0.6$ . The discharge voltage is about 3.4 V, high enough for large-scale application, but not high enough to decompose the electrolyte during recharge. However, the low electronic conductivity results in low kinetics and hence small current densities. This can be partially overcome by increasing the temperature, but this might increase electrolyte decomposition. The low kinetics and their improvement at elevated temperature have been discussed previously [4,5]. Ravet et al [6] showed that with a conductive carbon coating, full capacity could be attained at  $80^\circ\text{C}$  at  $\text{C/1}$  current density.

We demonstrated the possibility of synthesizing  $\text{LiFePO}_4$  via hydrothermal synthesis in just a few hours [7,8]. When this hydrothermal material was coated with sucrose following the Ravet method [9], good cycling behavior was observed at 60% capacity and a current density of  $0.14 \text{ mA/cm}^2$ . However, a recent study showed that in the hydrothermal material there is some disorder of the lithium and iron atoms resulting in poor behavior of the as-synthesized material [10].

Nazar's group [11] used a carbon gel technology to optimize  $\text{LiFePO}_4$  and showed that it could be cycled with 80% capacity at a  $2\text{C}$  current density at ambient temperature. We have reproduced their results [10]. Dominko [12] recently showed that with a novel carbon coating by aqueous gelatin solution,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCoO}_2$  had better performance, and the polarization was reduced. Here we used the same technology for  $\text{LiFePO}_4$  and demonstrated that 70% capacity was available at  $1.0 \text{ mA/cm}^2$  density.

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## EXPERIMENTAL

LiFePO<sub>4</sub> was prepared hydrothermally as previously reported by us [7] (material A), the sample was then coated with carbon [7] (material B). In order to prepare LiFePO<sub>4</sub> (material C) by high temperature, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (Alfa-Aesar) was ground, mixed stoichiometrically with CH<sub>3</sub>COOLi (Aldrich) and FeC<sub>2</sub>O<sub>4</sub>•2H<sub>2</sub>O (Aldrich), ground for 10 min, then pressed into pellets and heated at 350°C in a tube furnace in flowing helium gas for 4 h. After slowly cooling to room temperature, the gray soft pellets were reground for 10 min, pressed into pellets again, heated slowly to 700°C, and kept there for 10 h. The sample was ground after cooling to room temperature before use.

In order to remove the moisture from material A, it was heated in a tube furnace in flowing helium at 350°C for 4 h. Material C was used as prepared. Both materials were reacted with bromine (Fisher) in acetonitrile solution for up to 5 d. The final compound was washed with acetonitrile several times to remove the impurities, then dried in a vacuum oven overnight at 100°C. The materials were analyzed using XRD on a Scintag diffractometer to identify the phases present.

**Carbon Coating:** 17 mg and 9 mg gelatin (Type A, Aldrich) were dissolved in 30 ml and 10 ml water respectively and 2 drops of 0.05 M LiOH solution were added to the 30 ml solution resulting in a pH of 8.85. 1.02 g LiFePO<sub>4</sub>, 82 mg carbon black and 2 ml 0.05 M LiCl were added to this solution with stirring. Then the 10 ml solution was added and the beaker was put on a hot plate with spinning bar until almost all the water was gone. The sample was dried in a vacuum oven at 100°C overnight.

The electrodes were prepared by mixing the LiFePO<sub>4</sub> composite formed above with carbon black, and Teflon in the weight ratio 85:10:5 and grinding the slurry with 2 drops of hexane in a mortar. A thin film was made, which was hot pressed into an Exmet grid at a typical loading of 15 mg/cm<sup>2</sup>. The electrolyte was a 1M solution of LiPF<sub>6</sub> in a 1:1 volume ratio of dimethylcarbonate and ethylenecarbonate (EM, Industries). Only the weight of the LiFePO<sub>4</sub> was included for calculating the capacity. All of the data were collected on a MacPile system at ambient temperature (25°C).

## DISCUSSION

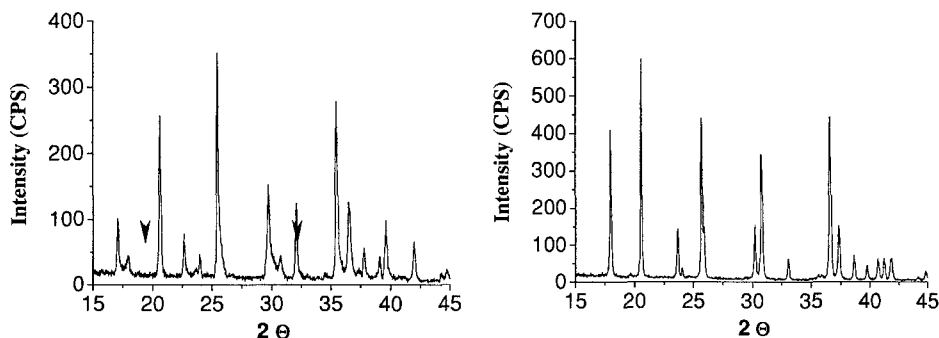
Rietveld structure refinements were performed on materials A, B and C. The refinements reveals the presence of iron in the lithium sites, for which Fe/Li ratio was refined as shown in Table I. The FePO<sub>4</sub> was prepared by the bromine delithiation of material C.

**Table I.** Rietveld refinements for LiFePO<sub>4</sub> materials A, B, C and FePO<sub>4</sub>.

	LiFePO <sub>4</sub> (A)	LiFePO <sub>4</sub> (B)	LiFePO <sub>4</sub> (C)	FePO <sub>4</sub>
<b>a (Å)</b>	10.381	10.351	10.333	9.837
<b>b (Å)</b>	6.013	6.018	6.011	5.799
<b>c (Å)</b>	4.716	4.713	4.696	4.790
<b>Fe on Li site</b>	0.08	0.05	0.0	0.0
<b>R<sub>i</sub></b>	3.4%	2.8%	2.7%	3.9%
<b>R<sub>p</sub></b>	10.21%	8.94%	8.65%	9.19%

DCP-AES for material A showed that the Li, Fe, P atomic ratios are 0.83:1.07:1. This 7% excess iron is consistent with the Rietveld determination of 7-8% iron on the lithium sites.

The X-ray parameters of material C are consistent with the results reported by Thomas [13]. The mechanism for the iron substitution in materials A and B is not known. Because the size of  $\text{Fe}^{2+}$  (0.78 Å) is larger than  $\text{Li}^+$  (0.60 Å), when lithium is partly substituted by iron, the lattice is larger. The ordering of the Li and Fe in the high temperature synthesized  $\text{LiFePO}_4$  is essentially perfect with no disorder detected by the Rietveld analysis. For materials A and B, the iron on the lithium sites probably partially blocks the pathway for the diffusion of lithium, even during the oxidation by liquid bromine. Figure 1 shows the XRD for  $\text{LiFePO}_4$  (A and C) after reaction with bromine.

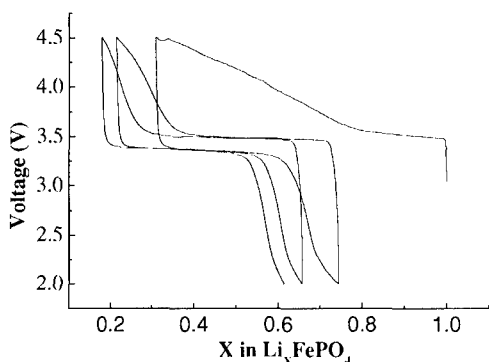


**Figure 1.** XRD of materials A and C after reaction with  $\text{Br}_2$ , arrows show the  $\text{FePO}_4$  phase in material A.

Material C was converted to  $\text{FePO}_4$  easily and no  $\text{LiFePO}_4$  was observed in the XRD, but for material A, even after 5 d, the major phase was still  $\text{LiFePO}_4$ , with a small amount of  $\text{FePO}_4$ . This difference can be explained if the iron atoms block the diffusion of lithium during the oxidation.

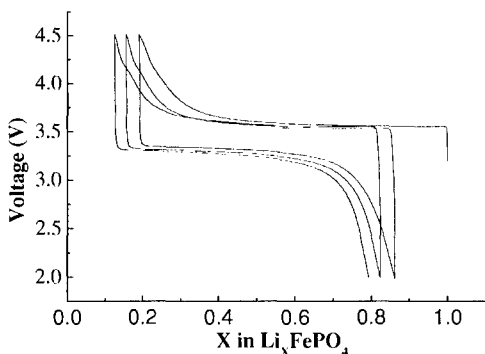
The electrochemistry of the hydrothermal  $\text{LiFePO}_4$  carbon coated using sucrose (material B) is shown in figure 2. Here the capacity was only about 60% of the theoretical value even at low current density. And the profile shifted to the left, probably as more lithium was removed from the sample. During the first recharge, much of the lithium removal occurs at elevated potentials; as this behavior is not observed on subsequent cycles some atomic re-organization may be occurring. The flat recharge/discharge curve after the initial recharge is typical of a two-phase system. The maximum capacity of under 80% is related to the maximum lithium content of around 0.8 per phosphorus, due to the excess iron atoms on the lithium sites.

The electrochemistry of material A is lower than that of material B, even at current density as low as  $0.03 \text{ mA/cm}^2$ , with only 40-45% capacity could be obtained and both the discharge and recharge curves were sloped following the first cycle with large polarization.



**Figure 2.** The first three cycles of  $\text{LiFePO}_4$  at current density  $0.14 \text{ mA/cm}^2$ , after [7].

Figure 3 shows the electrochemistry of  $\text{LiFePO}_4$  with the carbon black coating. At a high current density of  $1 \text{ mA/cm}^2$ , 80% of the lithium is removed on the first charge, and 0.7 Li are subsequently cycled giving a capacity of  $120 \text{ mAh/g}$ . The high current leads to a large polarization. In contrast to the iron rich material shown in Figure 2, the sloping potential on the first charge is much reduced. This is probably related to the perfect ordering of the Fe and Li ions. The 0.7 Li cycling capacity can be increased by reducing the current density. This is consistent with the data from SONY that showed only a 3% capacity loss for a current density of  $0.12 \text{ mA/cm}^2$  in a button cell configuration [2].



**Figure 3.** The first three cycles of  $\text{LiFePO}_4/\text{C}$  at current density  $1.0 \text{ mA/cm}^2$ .

The good performance of this system was achieved with a 15% carbon in the cathode structure. We are currently working on optimizing the carbon content by understanding its nano-structure so that minimum quantities can be used.

## CONCLUSIONS

The very good electrochemical behavior of  $\text{LiFePO}_4$ , which combined with its low cost, makes it an excellent candidate for an intermediate capacity cathode replacement for  $\text{LiCoO}_2$  until cathodes with capacities over 200 mAh/g are developed. Hydrothermal synthesis leads to iron disorder and excess iron in the structure, which degrades its electrochemical performance relative to high temperature formed materials. This may be partially corrected by a subsequent high temperature heating with carbon. High temperature formed  $\text{LiFePO}_4$ , carbon coated from gelatin, demonstrated more than 70% capacity even at current densities of 1 mA/cm<sup>2</sup>.

## ACKNOWLEDGMENTS

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